Metallacyclopentane Formation: A Deactivation Pathway for a Tungsten(VI) Alkylidene Complex in Olefin Metathesis Reactions

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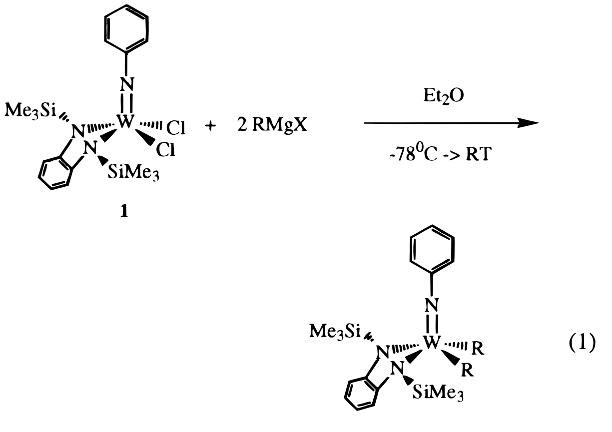
$W(NPh)[o-(Me_3SiN)_2C_6H_4](CH_2CMe_3)_2$, **2h**, is quantitatively converted to a new metallacyclopentane complex, $W(CH_2CH_2CH_2CH_2)(NPh)[o-(Me_3SiN)_2C_6H_4]$, **4**, upon the addition of ethylene at $T > 70$ °C. The complex $W(CH_2CH_2CH_2CH_2)(NPh)[o-(Me_3SiN)_2C_6H_4]$, **4**, was also formed by the transmetalation reaction of $W(NPh)[o-(Me_3SiN)_2C_6H_4](Cl)_2$ with the corresponding Grignard reagent, $BrMg(CH_2)_4MgBr$, and also when $W(NPh)[o-(Me_3SiN)_2C_6H_4](PMe_3)({=}C(H)t\text{-Bu})$, **3**, reacts with ethylene. Mechanistic studies suggest that **2h** and **3** react with ethylene through a common base-free alkylidene intermediate which undergoes metathesis with ethylene and then generates a W(IV) intermediate which is converted to **4** by coupling two molecules of ethylene. This reaction is a deactivation pathway when **3** is used as an olefin metathesis catalyst for terminal olefins because ethylene is generated during the reaction. The tungsten(IV) complex $W(NPh)[o-(Me_3SiN)_2C_6H_4](PMe_3)_2(\eta^2\text{-}C_2H_4)$, **5**, was observed during the reaction between **3** and ethylene. Complex **5** can also be synthesized from the diethyl complex $W(NPh)[o-(Me_3SiN)_2C_6H_4](CH_2CH_3)_2$, **2b**, in the presence of PMe_3. Addition of excess ethylene to **5** gives **4**. The X-ray structure of **4** was determined.

Introduction

Recent work[1,2] in our group has successfully used *N,N′*-bis (trimethylsilyl)-*o*-phenylenediamide, $[o-(Me_3SiN)_2C_6H_4]^{2-}$, TMS_2pda, as an ancillary ligand for a variety of tungsten(VI) complexes. The facile synthesis of $W(NPh)R_2[o-(Me_3SiN)_2C_6H_4]$, **2(a−j)**, from $W(NPh)Cl_2[o-(Me_3SiN)_2C_6H_4]$, **1**, (eq 1) for a wide range of alkyl groups has allowed us to begin to explore the chemistry of this class of d^0 dialkyl complexes. For example, the alkylidene complex $W(NPh)[o-(Me_3SiN)_2C_6H_4](CHCMe_3)(PMe_3)$, **3**, can be synthesized via an α-H abstraction when **2h** is heated in the presence of PMe_3.[1c,3]



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(1)

2a-j R = Me, Et, *n*-Pr, *i*-Bu, Ph, CH2Ph, (CH2)2Ph, CH2CMe3, CH2CMe2Ph, CH2SiMe3

In this paper, we report that the reaction of **2h** or **3** with ethylene results in the formation of a metallacyclopentane complex via an olefin metathesis initiated pathway. Mechanistic aspects of the transformation of **3** into the metallacyclopentane complex $W(CH_2CH_2CH_2CH_2)(NPh)[o-(Me_3SiN)_2C_6H_4]$, **4**, are discussed, and the reaction is shown to proceed through the W(IV) ethylene complex $W(C_2H_4)(NPh)[o-(Me_3SiN)_2C_6H_4](PMe_3)_2$, **5**. The formation of a metallacyclopentane complex when **3** reacts with ethylene is the likely deactivation pathway for **3** when **3** is used as a catalyst for the metathesis of terminal olefins. Compounds **4** and **5** have been isolated and structurally characterized by single-crystal X-ray diffraction techniques.

Results and Discussion

Reaction of 2h with Ethylene. We have demonstrated that the thermolysis reaction of complex **2h** in the presence of PMe_3 at 80 °C affords the alkylidene complex $W(NPh)[o-(Me_3SiN)_2C_6H_4](CHCMe_3)(PMe_3)$, **3**, which has proven to be a catalyst precursor for ring-opening metathesis polymerization (ROMP) of norbornene and cyclooctene.[1c,d] In contrast, complex **2a** forms an adduct $W(NPh)[o-(Me_3SiN)_2C_6H_4](Me)_2(PMe_3)$ upon the addition of PMe_3 but undergoes no further reaction in the presence of PMe_3 even under more vigorous conditions. Although complex **2a** does not

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(1) (a) Wang, S.-Y. S.; Abboud, K. A.; Boncella, *J. Am. Chem. Soc.* **1997**, *119*, 11990. (b) Huff, R. L.; Wang, S.-Y. S.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1997**, *16*, 1779. (c) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3378. (d) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Polym. Prepr.* **1994**, *35*, 691.

(2) Boncella, J. M.; Wang, S.-Y. S.; VanderLende, D. D.; Huff, R. L.; Vaughan, W. M.; Abboud, K. A. *J. Organomet. Chem.* **1997**, *530*, 59.

(3) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 11015.

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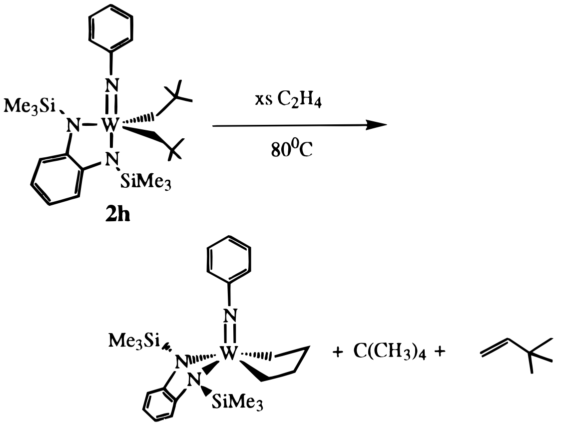
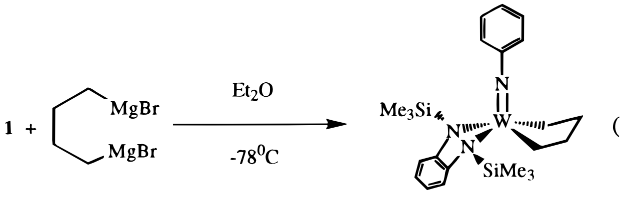
react with ethylene, complex **2h** reacts with ethylene at 80 °C to form the metallacyclopentane complex $W(CH_2CH_2CH_2CH_2)(NPh)[o\text{-}(Me_3SiN)_2C_6H_4]$, **4**, with the loss of neopentane and *tert*-butylethylene (eq 2).



(2)

4

Synthesis of 4. The metallacyclopentane complex **4** was synthesized independently on a preparative scale by allowing the dichloride complex $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](Cl)_2$, **1**, to react with $BrMg(CH_2)_4MgBr$ (eq 3).[4] Compound **4** was characterized by NMR spectroscopy and via a single-crystal X-ray diffraction study. The ^1H NMR spectrum of **4** in benzene-d_6 displays broad resonances with unresolved fine structure that are assigned to the CH_2 protons of the metallacycle ring at 2.93, 2.91, 2.42, and 1.54 ppm, respectively, in a 2:2:2:2 ratio. The trimethylsilyl protons were observed as a sharp singlet at 0.28 ppm, as is consistent with a square pyramidal geometry in which a mirror plane contains the imido ligand and tungsten atom and bisects the N−W−N and C−W−C angles. The $^{13}C\{^1H\}$ NMR of **4** displays resonances at δ 61.25 ($^1J_{W-C} = 73.6$ Hz, $^1J_{C-H} = 122.9$ Hz) and δ 35.23 ($^1J_{C-H} = 124.3$ Hz) that are assigned to C_α and C_β of the metallacycle, respectively. The ^{13}C spectral parameters are similar to known tungstacyclopentane complexes.[5]



(3)

4

A single crystal of **4** suitable for an X-ray structure determination was grown by cooling a pentane solution to −20 °C. General data collection and refinement data are listed in Table 1. A thermal ellipsoid plot of complex **4** along with the atom-labeling scheme is given in Figure 1, while selected bond lengths and angles are presented in Table 2. The coordination geometry around the W atom is that of a slightly distorted square pyramid. In this structure, the imido N occupies the axial site while the N atoms of the TMS$_2$pda ligand and the C atoms of the metallacyclopentane group form the basal plane. The tungsten atom resides 0.717 Å above the plane defined by N(1), N(2), C(1), and C(4) (mean deviation is

Table 1. Crystallographic and Data Collection Parameters for $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](CH_2CH_2CH_2CH_2)$, 4, and $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](PMe_3)_2(\eta^2\text{-}C_2H_4)$, 5

	5	**4**
A. Crystal Data (173 K)		
a, Å	36.2551(8)	10.3249(1)
b, Å	13.5914(4)	18.1030(2)
c, Å	13.9794(4)	13.8308(2)
β, deg	90.0	103.210(1)
V, Å^3	6888.5(3)	2516.73(5)
d_{calc}, g cm^{-3} (173 K)	1.450	1.535
empirical formula	$C_{26}H_{49}N_3P_2Si_2W\cdot{}^1/_2C_7H_8$	$C_{22}H_{35}N_3Si_2W$
fw	751.72	581.56
cryst system	orthorhombic	monoclinic
space group	*Pbcn*	$P2_1/n$
Z	8	4
F(000), electrons	3064	1160
cryst size (mm^3)	0.44 × 0.38 × 0.10	0.45 × 0.34 × 0.06
B. Data Collection (173 K)		
radiation, λ (Å)	Mo Kα, 0.710 73	
mode	ω-scan	
scan width and rate	0.3 deg/frame and 30 s/frame	
2θ range, deg	3−55	3−55
range of *hkl*	$-24 \le h \le 50$ $-11 \le k \le 18$ $-19 \le l \le 7$	$-12 \le h \le 12$ $0 \le k \le 23$ $0 \le l \le 17$
tot. reflcns measd	27 782	12 840
unique reflcns	7881	5197
abs coeff, μ(Mo Kα), mm^{-1}	3.539	4.697
C. Structure Refinement		
refinement method	full-matrix least-squares on F^2	
S, goodness-of-fit[a]	1.20	1.06
no. of variables	341	253
R_1/reflcns[a]	3.80/7180 > 2σ(*I*)	3.49/4443 > 2σ(*I*)
wR_2/reflcns[a]	8.27/7784	8.11/5144
R_{int} (%)	3.34	6.22
max shift/esd	0.001	0.001
min peak in diff Four. map (e Å^{-3})	−2.32	−1.38
max peak in diff Four. map (e Å^{-3})	1.19	0.92

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$, $p = [\max(F_o^2,0) + 2F_c^2]/3$.

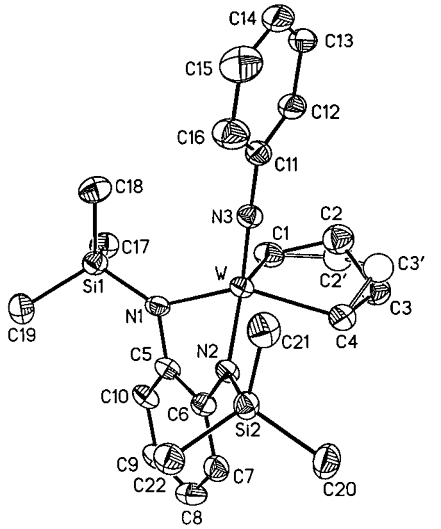


Figure 1. Molecular structure of $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](CH_2CH_2CH_2CH_2)$, **4**, with 50% probability ellipsoids and showing the atom-numbering scheme. All hydrogen atoms are omitted for clarity. The metallacyclopentane ring is disordered by the flipping of the five-membered ring, denoted by W−C(1)−C(2)−C(3)−C(4) and W−C(1)−C(2′)−C(3′)−C(4).

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[4] The Grignard reagent, $BrMg(CH_2)_4MgBr$, was obtained by reacting $Br(CH_2)_4Br$ (purchased from Aldrich) with Mg metal.

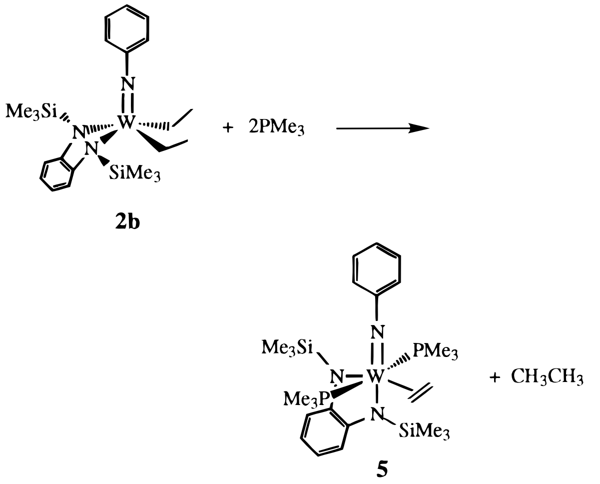
[5] Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for W(NPh)[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$](CH$_2$CH$_2$CH$_2$CH$_2$), 4

W−N(1)	2.023(4)	W−C(1)	2.182(5)
W−N(2)	2.004(4)	W−C(4)	2.183(5)
W−N(3)	1.736(4)		
N(1)−W−N(2)	84.1(2)	N(2)−W−C(4)	85.5(2)
N(1)−W−N(3)	118.1(2)	N(3)−W−C(1)	99.8(2)
N(1)−W−C(1)	86.3(2)	N(3)−W−C(4)	102.0(2)
N(1)−W−C(4)	138.4(2)	C(1)−W−C(4)	76.1(2)
N(2)−W−N(3)	119.5(2)	C(11)−N(3)−W	174.0(3)
N(2)−W−C(1)	139.3(2)		

0.001 Å). The W−C(1) and W−C(4) bond lengths (2.182(5), 2.183(5) Å, respectively) are within the range expected for W(VI)−C distances.[2,6] The W−N$_{imido}$ bond length is 1.736(4) Å and is consistent with a W−N triple bond.[7,8] The geometry about the N atoms of the [*o*-(Me$_3$SiN)$_2$C$_6$H$_4$]$^{2-}$ ligand is planar as is observed in silylamines.[9] The ligand is folded about the N−N vector which causes the SiMe$_3$ groups to be displaced above the basal plane. The folding of the ligand also tilts the N coordination planes by 60−65° relative to the basal plane of the molecule.

The formal electron count at the metal center could be as high as 18e$^-$ if both sets of nitrogen lone pairs of the [*o*-(Me$_3$SiN)$_2$C$_6$H$_4$]$^{2-}$ ligand can be donated to the metal center. Donation of both amide lone pairs is not possible since there are only three d orbitals that are of the proper symmetry to form π bonds with the ligands. Given that the d_{xz} and d_{yz} orbitals form the π bonds with the imido group, only the d_{xy} orbital is available to overlap with the N π electrons on the diamido ligand. Thus, the maximum electron count at the metal center is 16e$^-$. Furthermore, the structure of **4** shows that the folding of the diamide ligand brings the p orbitals on the nitrogen atoms to within only ca. 25−30° of the *xy* plane, preventing efficient overlap between the d_{xy} orbital and the N lone pairs. The structural constraints imposed by the chelating nature of the [*o*-(Me$_3$SiN)$_2$C$_6$H$_4$]$^{2-}$ ligand lead us to suggest that **4** and the other square pyramidal dialkyl complexes[2] are best described as 14e$^-$ or at most 16e$^-$ compounds.



(4)

Synthesis of 5. The W(IV) ethylene complex, **5**, an intermediate observed in the reaction of **3** with ethylene, was synthesized independently on a preparative scale by allowing the diethyl complex W(NPh)[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$](CH$_2$CH$_3$)$_2$, **2b**, to react with trimethylphosphine (eq 4).[1a] In the ^{1}H NMR spectrum of **5**, the two multiplets at 1.96 and 2.19 ppm are assigned the ethylene protons, while the two equivalent PMe$_3$ protons are reasponsible for the resonance at 1.05 ppm. The trimethylsilyl protons are observed as two broad peaks at 0.28 and 0.61 ppm, indicating their chemical inequivalence. The gated, coupled, ^{13}C NMR spectrum reveals a triplet resonance at 36 ppm corresponding to the ethylene carbon atoms with $^1J_{C-H} = 156$ Hz, indicating some "metallacyclopropane" character.[10]

The structure of complex **5** was verified by a single-crystal X-ray diffraction study. A thermal ellipsoid plot of **5** with the atom-labeling scheme is given in Figure 2, while selected bond lengths and angles are presented in Table 3. The coordination geometry around the W atom is that of a slightly distorted octahedron. In this structure, the imido nitrogen atom and one of the amide nitrogen atoms occupy *trans* sites, while the phosphines are also *trans* with respect to each other. The W−N$_{imido}$ bond length is 1.784(4) Å and is consistent with a W−N triple bond making **5** an 18e$^-$ complex.[7,8] The W−N(1) and W−N(2) bond lengths (2.154(4), 2.160(3) Å) are essentially the same which is surprising since this implies that the imido group does *not* exert a significant *trans* influence on the W−N(1) bond. It appears that the steric bulk of the two trimethylphosphine ligands prevents an asymmetric approach of the amido N atoms to the W center causing an increase in the expected W−N(2) bond length.

A comparison of the W−N$_{amide}$ bond lengths in **5** with the six coordinate dialkyl complex W(NPh)(CH$_3$)$_2$[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$](PMe$_3$) reveals that W−N(2) in **5** is 0.1 Å longer that the W−N$_{amide}$ bonds (both cis to the imido group) in W(NPh)(CH$_3$)$_2$[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$](PMe$_3$).[2] The related five coordinate complex, **2h**, has a trigonal bipyramidal structure with axial imido and amide groups, while one amide and the two neopentyl groups occupy the equatorial plane. The axial W−N$_{amide}$ and equatorial W−N$_{amide}$ lengths[2] are 1.98 and 2.13 Å, respectively, and suggest that in the absence of other steric influences, the strong trans influence of the imido group results in very different W−N $_{amide}$ distances.

The ethylene group coordinates cis to the imido ligand, as observed in other d^2 ethylene complexes that have imido coligands reported by Schrock[11] and Niel-

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(6) (a) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454. (b) Fischer, J.; Kress, J.; Osborn, J. A.; Ricard, L.; Wesolek, M. *Polyhedron* **1987**, *6*, 1839. (c) Zhang, C.; Schlemper, E. O.; Schrauzer, G. N. *Organometallics* **1990**, *9*, 1016. (d) Eagle, A. A.; Young, C. G.; Tiekink, E. R. T. *Organometallics* **1992**, *11*, 2934. (e) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (f) Fletcher, S. R.; Skapski, A. C. *J. Organomet. Chem.* **1973**, *59*, 299. (g) Faller, J. W.; Kucharczyk, R. R.; Ma, Y. *Inorg. Chem.* **1990**, *29*, 1662. (h) Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Trotter, J.; Veltheer, J. E.; Yee, V. C. *Organometallics* **1992**, *11*, 3104. (i) van der Schaaf, P. A.; Abbenhuis, R. A. T. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1993**, 504.

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(8) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

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(11) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077.

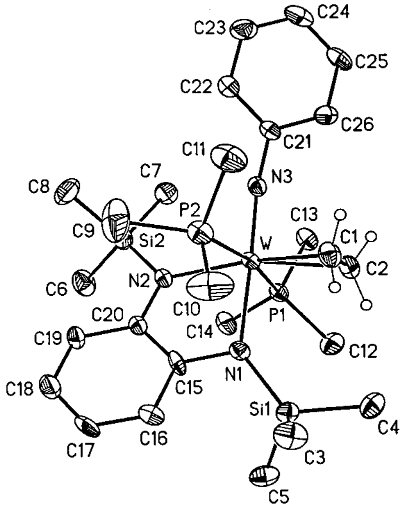

Figure 2. Molecular structure of W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$](η^2-C_2H_4)$(PMe_3)_2$, **5**, with 50% probability ellipsoids and showing the atom-numbering scheme. All hydrogen atoms, except those on the η^2-ethylene, are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]$(PMe_3)_2$(η^2-C_2H_4), 5

W−N(1)	2.154(4)	W−P(2)	2.564(1)
W−N(2)	2.160(3)	W−C(1)	2.234(5)
W−N(3)	1.784(4)	W−C(2)	2.223(5)
W−P(1)	2.562(1)	C(1)−C(2)	1.434(6)
N(1)−W−N(2)	78.60(14)	N(3)−W−P(1)	94.40(12)
N(1)−W−N(3)	175.9(2)	N(3)−W−P(2)	89.64(12)
N(1)−W−P(1)	89.66(10)	N(3)−W−C(1)	91.2(2)
N(1)−W−P(2)	86.26(10)	N(3)−W−C(2)	89.8(2)
N(1)−W−C(1)	87.7(2)	P(1)−W−P(2)	170.27(4)
N(1)−W−C(2)	91.8(2)	P(1)−W−C(1)	113.19(13)
N(2)−W−N(3)	101.2(2)	P(1)−W−C(2)	75.92(13)
N(2)−W−P(1)	84.42(10)	P(2)−W−C(1)	75.50(13)
N(2)−W−P(2)	86.12(10)	P(2)−W−C(2)	113.00(13)
N(2)−W−C(1)	157.8(2)	C(1)−W−C(2)	37.5(2)
N(2)−W−C(2)	158.2(2)	C(21)−N−W	170.3(3)

son.[12] The ethylene ligand is oriented with the C atoms in the W−P−N(2)−P plane in order to maximimize back-donation from the d_{xy} orbital to the ethylene π^* orbital. The observation of two resonances for the ethylene protons in the ^1H NMR spectrum of **5** at room temperature is consistent with slow rotation of the ethylene and indicates that a strong π bond exists between W and ethylene. The C(1)−C(2) bond length, 1.434(6) Å, is in the middle of the range of C−C bond lengths observed in other d^2 olefin complexes,[13] while the W−C(1) and W−C(2) bond lengths of 2.234(5) and 2.223(5) Å are similar to those of other W(IV) olefin complexes that have been structurally characterized.[12b,13c,e]

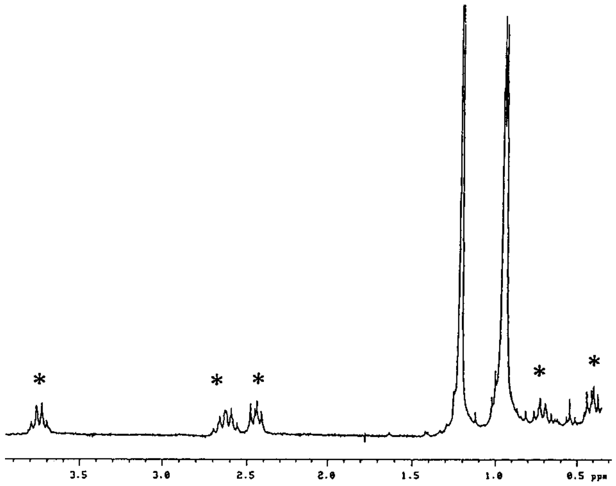

Figure 3. Partial ^1H NMR spectrum of W(NPh)[*o*-$Me_3SiN)_2C_6H_4$](CH^{t}BuCH_2CH_2), **8** (300 MHz, room temperature, benzene-d_6, *'s indicate five ring protons).

Mechanism of the Formation of 4 from 2h and 3. The observation that the reaction between **2h** and ethylene produces neohexene and neopentane along with **4** suggested to us that the formation of **4** is likely to proceed through a metathetical pathway. This is reasonable because neopentane is the product of α-H abstraction to form a neopentylidene complex and neohexene is the first product formed when a neopentylidene complex undergoes productive metathesis with ethylene. Previously,[3] we had established that, upon heating complex **2h**, α-H abstraction to form the base free neopentylidene complex is the predominant reaction pathway. In the presence of PMe_3, complex **3** is isolated, while in the absence of PMe_3 a reversible metalation of one of the Me_3Si groups of the *o*-$(Me_3SiN)_2C_6H_4$ ligand occurs.[3] Given that **3** is readily synthesized and isolated and that dissociation of PMe_3 from **3** in solution is a rapid process, we examined the reaction between **3** and ethylene in order to determine whether complex **4** would be formed.

When **3** was allowed to react with ethylene at room temperature in an NMR tube, an intermediate, W(CH*t*-BuCH_2CH_2)(NPh)[*o*-$(Me_3SiN)_2C_6H_4$], **8**, was observed before any neohexene was produced. The ^1H NMR spectrum of **8** (Figure 3) shows five multiplet resonances at 0.39, 0.71, 2.45, 2.61, and 3.75 ppm in a 1:1:1:1:1 ratio, which account for the five ring-protons of the metallacycle. In the $^{13}C\{^1H\}$ NMR spectrum, three singlets were observed at 77.6 (J_{W-C} = 56 Hz), 38.8 (J_{W-C} = 49.4 Hz), and 25.1 ppm which are assigned to the metallacycle carbon atoms. Further investigation by 2D NMR ($^1H-^1H$ homonuclear and $^{13}C-^1H$ heteronuclear correlation experiments) has allowed us to assign all the proton and carbon resonances of **8**. The proton at 0.39 ppm is attached to C_α (77.6 ppm, *tert*-butyl-substituted carbon), the two multiplets at 0.71 and 2.45 ppm arise from the protons bonded to $C_{\alpha'}$ (38.8 ppm), and the most downfield protons at 2.61 and 3.75 ppm are assigned as the β-protons of the metallacyclobutane ring. The observation that the β-protons appear at the most downfield chemical shifts is consis-

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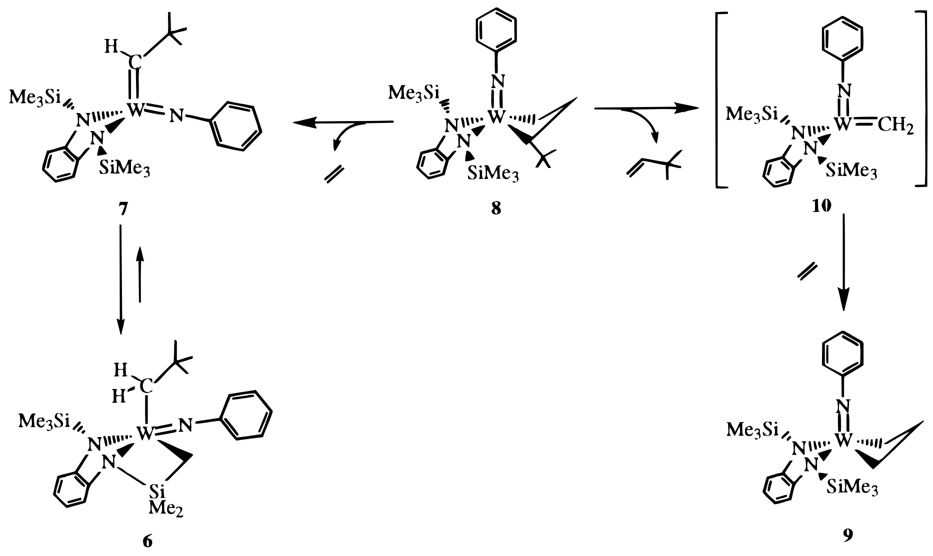
[12] (a) Clark, G. R.; Nielson, A. J.; Richard, C. E. F.; Ware, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 1173. (b) Clark, G. R.; Nielson, A. J.; Richard, C. E. F.; Ware, D. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1343.

[13] (a) Rietveld, M. H. P.; Teunissen, W.; Hagen, H.; ven de Water, L.; Grove, D. M.; van der Schaaf, P. A.; Mühlebach, A.; Kooijman, H.; Smeets, W. J. J.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 1674. (b) Fernández, F. J.; Gómez-Sal, P.; Maneanero, A.; Royo, P.; Jacobson, H.; Berke, H. *Organometallics* **1997**, *16*, 1553. (c) Fanwick, P. E.; Rothwell, I. P.; Kriley, C. E. *Polyhedron* **1996**, *15*, 2403. (d) Wehman-Ooyevaar, I. C. M.; Kapteijn, G. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. J. *J. Chem. Soc., Dalton Trans.* **1994**, 703. (e) Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545. (f) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. (g) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169. (h) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420.

Scheme 1



tent with observations on similar metallacyclobutane complexes.[14]

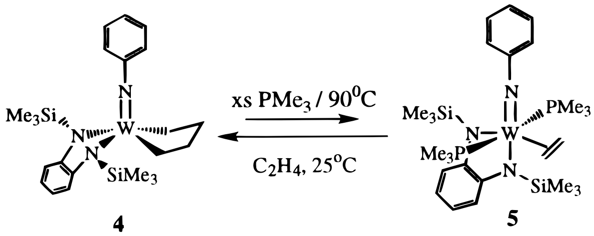
Attempts to synthesize and isolate complex **8** on a preparative scale were thwarted by the instability of **8** in solution. While crude **8** could be isolated as a solid by removing the solvent and PMe_3 under reduced pressure, the ^1H NMR spectrum of this material (C_6D_6 solution) revealed that **8** readily loses ethylene or neohexene to generate the metalated complex **6** or the unsubstituted metallacyclobutane complex, **9**, respectively. Presumably, loss of ethylene gives the base free neopentylidene complex which rapidly metalates (Scheme 1), while loss of neohexene leads to **9** via an intermediate methylidene complex which is scavenged by the ethylene produced in the formation of **6**.

When complex **3** was allowed to react with an excess of ethylene at room temperature for 4 days, two products were observed in a 44:56 ratio by ^1H NMR spectroscopy. One set of peaks (44%) were found at 3.89 (m, $2H_\alpha$), 2.86 (m, $1H_\beta$), 2.90 (m, $1H_\beta$), and 2.59 (m, $2H_\alpha$) ppm and were assigned to the metallacyclobutane $W(NPh)[(Me_3SiN)_2C_6H_4](CH_2CH_2CH_2)$, **9**. The structure of **9** is either square pyramidal or the compound is undergoing a rapid interconversion between square pyramidal and trigonal bipyramidal geometries because only one singlet was observed at 0.31 ppm for the trimethylsilyl groups.

The other set of peaks (56%) were observed at 1.94 (2H) and 2.17 (2H) ppm. This product was shown to be the tungsten(IV) complex $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](PMe_3)_2(\eta^2\text{-}C_2H_4)$, **5**, by comparison with the spectrum of an authentic sample which was obtained from the reaction between **2b** and excess PMe_3 (as described above). We propose that the unstable methylidene complex undergoes bimolecular coupling of methylidene ligands to give ethylene and a tungsten(IV) complex, which then was trapped by phosphines and ethylene to form compound **5** (Scheme 2). Formation of a W(IV) intermediate from **9** via a β-H elimination/reductive elimination process does not appear to occur though it is an attractive mechanistic pathway. Thus, we have not observed the formation of propene during the reaction of **3** with ethylene under any conditions.

In the presence of excess ethylene, both **9** and **5** are converted to the more stable metallacyclopentane complex $W(CH_2CH_2CH_2CH_2)(NPh)[(Me_3SiN)_2C_6H_4]$, **4** (>95% by NMR). The formation of complex **4** arises from the oxidative coupling of 2 equiv of ethylene to the tungsten(IV) complex.[15] The relative concentrations of all the intermediates as a function of time is shown in Figure 4. In a separate experiment, complex **5** was cleanly converted to **4** within several days, upon the addition of ethylene. This suggests that the formation of **4** from **3** is inevitable in the presence of ethylene.

To investigate the reversiblilty of the formation of **4** from **5**, **4** was allowed to react with trimethylphosphine. No reaction was observed within a few days at room temperature. However, when the reaction mixture was heated to 90 °C, **4** was slowly (60% conversion after 10 days; 91% after 30 days) converted to **5** with the loss of ethylene (eq 5). This experiment clearly shows the preferential formation of the W(VI) metallacyclopentane product. The fact that compound **2a** does not react with ethylene even at elevated temperatures provides further indirect evidence that the formation of **4** from **2h** proceeds through a neopentylidene intermediate.



(5)

Experiments using **3** as a metathesis catalyst for 1-pentene (40 equiv) show 90% conversion to 4-octene after 8 h at 80 °C as well as the formation of neohexene and **4** as the only observable metal-containing product. This is to be expected since the productive metathesis

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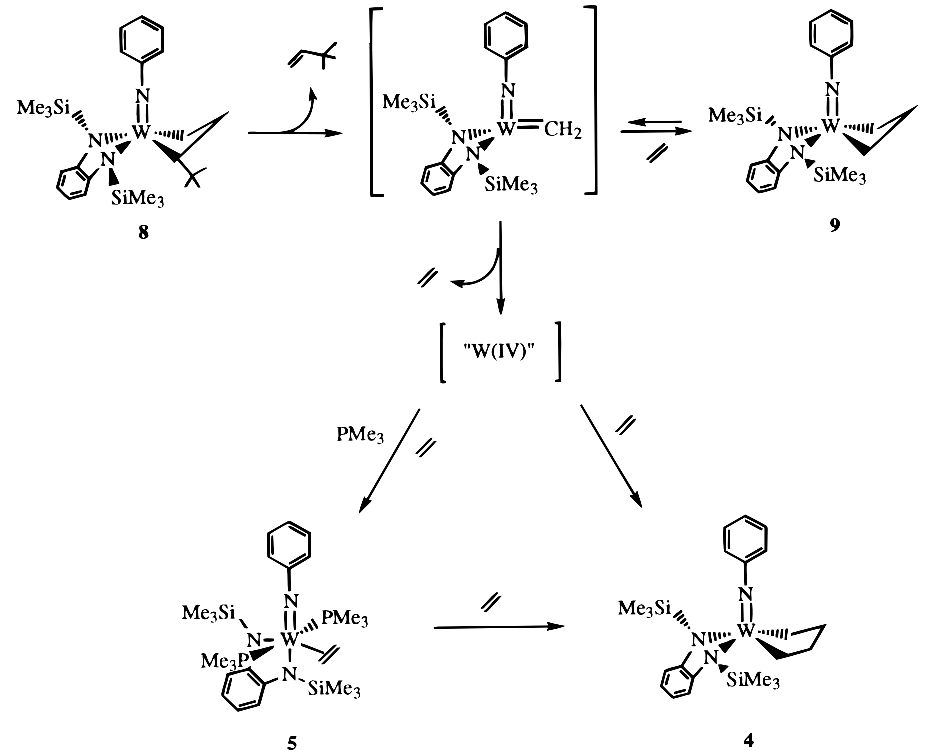
[14] (a) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535. (b) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

[15] (a) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558. (b) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7416.

Scheme 2



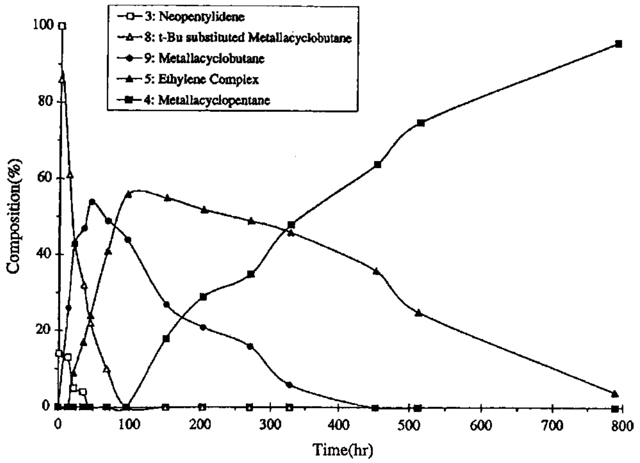


Figure 4. Relative amounts of **3**–**5**, **8**, and **9** as a function of time during thermolysis of **3** in the presence of ethylene.

of terminal olefins always gives ethylene as one of the products. Thus, the ethylene that is produced reacts with **3** or other alkylidene complexes that are formed during the reaction and effectively deactivates the catalyst system by converting all of the W complexes in the system to **4** which is inactive for further metathesis.

It is worthwhile to note that the formation of 1-butene was not observed when **4** was heated to its decomposition temperature (ca. 150 °C). The formation of 1-butene from metallacyclopentanes of Pt,[16] Ti,[17] and Ta[18] has been reported to occur via a β-hydride elimination pathway. Recently, we have demonstrated that the mechanism of β-H transfer in the diethyl complex, **2b**, involves direct β-H *abstraction*,[1a] rather than β-H elimination. It is possible that complex **4** does not undergo decomposition via β-hydride transfer because the geometric constraints of the metallacyclopentane ring prevent the molecule from achieving the transition state necessary to effect transfer of a β-H atom directly to a carbon that is bound to the metal. As a result, the reactivity of **4** is apparently limited to disruption of the metallacyclopentane structure by expulsion of ethylene and reduction of the metal center.

Conclusions

The observation that ethylene reacts with the bis(neopentyl) complex, **2h**, at elevated temperatures to give the metallacyclopentane complex, **4**, is consistent with the proposal that this reaction actually occurs through a neopentylidene complex which is generated *in situ* during the reaction. The formation of **4** in the reaction of $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](CHCMe_3)(PMe_3)$, **3**, with ethylene confirms this proposal because **3** is an effective source of base free alkylidene through the dissociation of PMe_3. The conversion of the unsubstituted metallacyclobutane complex, **9**, to the W(IV) ethylene complex appears to proceed through the methylidene complex, **10**, and probably through a W(IV) intermediate both of which are not observed.

In related chemistry, a dimeric Mo(IV) complex has been isolated from the reaction of $Mo[N(2,6\text{-}i\text{-}Pr_2C_6H_3)][OCMe_3]_2(C(H)CMe_3)$ with ethylene.[19] The precursor of this Mo(IV) complex was proposed to be a Mo(VI) methylidene which reductively coupled giving ethylene

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[16] (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (b) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451.

[17] (a) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529. (b) McDermott, J. X.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 947.

[18] McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610.

[19] Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902.

and the observed dimeric Mo(IV) product. Changing the alkoxide ligands to $OCMe(CF_3)_2$ allowed the observation of an unstable metallacyclopentane complex, $Mo(CH_2CH_2CH_2CH_2)[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)][OCMe(CF_3)_2]_2$.[19] A similar process is possible in the present case, only the increased stability of W(VI) vs Mo(VI) facilitates the formation and isolation of the metallacyclopentane complex, **4**, via the oxidative coupling of two molecules of ethylene. Because PMe_3 is present in the system when **3** reacts with ethylene, the W(IV) PMe_3−olefin complex, **5**, is also initially formed. The conversion of **5** to **4** is somewhat surprising since it involves loss of PMe_3 in favor of coordination of ethylene; however, it is clear that stability of W(VI) relative to W(IV) is the driving force for the formation of **4**.

The formation of **4** from the alkylidene, **3**, also provides an explanation for the deactivation of **3** when **3** is used as an initiatior for the metathesis of terminal olefins. When terminal olefins undergo metathesis, ethylene is always produced. The presence of ethylene thereby provides a facile path for the deactivation of **3** via the formation of **4**. We would expect that metallacyclopentane formation would be most likely to occur when third-row transition metals are used as metathesis catalysts because of the propensity of these metals to form stable, high oxidation state complexes.

Experimental Section

General Procedures. All reactions were conducted under a dry argon atmosphere using standard Schlenk techniques or were performed in a nitrogen-filled drybox. Diethyl ether (Et_2O) was distilled from sodium benzophenone ketyl. Toluene, pentane, and hexane were distilled from sodium. The compounds **1** and **2a,b,f,h,j** were prepared as described previously.[2] NMR solvents were stored over molecular sieves and were degassed prior to use. ^1H NMR spectra were measured at 300 MHz on a Varian Gemini 300 or VXR 300 spectrometer with C_6D_6 and C_7D_8 as solvents. The chemical shifts are reported in parts per million downfield from tetramethylsilane ($\delta = 0$ ppm) and were referenced to residual C_6D_5H ($\delta = 7.15$ ppm) and C_7D_7H ($\delta = 2.09$ ppm) as internal standards. ^{13}C NMR spectra were recorded at 300 MHz on a Varian Gemini 300 or VXR 300 spectrometer with C_6D_6 and C_7D_8 as solvents, referenced to the central line of the solvents, and reported relative to tetramethylsilane. Elemental analyses (C, H, N) were performed by Atlantic Microlab, Inc., Norcross, GA.

Preparation of W(NPh)[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$](CH$_2$CH$_2$CH$_3$)$_2$, 2c. $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](Cl)_2$ (1.0 g, 1.68 mmol) was dissolved in Et_2O (100 mL) and cooled to −78 °C. Two equivalents of *n*-PrMgCl (1.7 mL, 3.4 mmol; 2.0 M solution in Et_2O) were then added by a syringe. The reaction was allowed to warm to room temperature and was stirred for 1 h, during which time a brown color appeared and salts precipitated. The solvent was then removed under reduced pressure, and the remaining brown-black oil was dried under reduced pressure for 3 h. The oil was then extracted with pentane and filtered by filter cannula until the filtrate was almost clear. The solvent was then removed under reduced pressure, and the remaining brown oil was dried under reduced pressure for 2 h. Yield: 78%. ^1H NMR (C_6D_6, δ): 0.53 (s, 18H, $-Si(CH_3)_3$, $^2J_{Si-H} = 6.6$ Hz); 1.30 (t, 6H, $-CH_2CH_2C\mathit{H}_3$); 1.92 (m, 2H, $-CH_2C\mathit{H}_2CH_3$); 2.06 (dt, 2H, $-C\mathit{H}_2CH_2CH_3$); 2.16 (m, 2H, $-CH_2C\mathit{H}_2CH_3$); 2.33 (dt, 2H, $-C\mathit{H}_2CH_2CH_3$); 7.09 (t, 1H, *p*-NPh-*H*); 7.27 (m, 2H, aromatic); 7.34 (t, 2H, *m*-NPh-*H*); 7.53 (d, 2H, *o*-NPh-*H*); 7.57 (m, 2H, aromatic). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 1.49 ($-Si(CH_3)_3$, $J_{C-H} = 119.3$ Hz); 21.79 ($-CH_2CH_2C\mathit{H}_3$, $J_{C-H} = 121.4$ Hz); 26.70 ($-CH_2\mathit{C}H_2CH_3$, $J_{C-H} = 132.2$ Hz); 69.29 ($-CH_2CH_2CH_3$, $J_{C-H} = 113.1$ Hz); 122.36, 124.08, 125.04, 125.77, 128.64, 134.48, 156.42 (aromatic).

Preparation of W(NPh)[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$](CH$_2$CH(CH$_3$)$_2$)$_2$, 2d. $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](Cl)_2$ (1.2 g, 2.01 mmol) was dissolved Et_2O (100 mL) and cooled to −78 °C. Two equivalents of *i*-BuMgCl (2.01 mL, 4.02 mmol; 2.0 M solution in Et_2O) were then added by a syringe. The reaction was allowed to warm to room temperature and was stirred for 1 h, during which time a brown color appeared and salts precipitated. The solvent was then removed under reduced pressure, and the remaining brown-black oil was dried under reduced pressure for 3 h. The oil was then extracted with pentane and filtered by filter cannula until the filtrate was almost clear. The solution was concentrated to about 10 mL and cooled to −78 °C for 3 h. The resulting golden-brown solid was isolated by filtration and was dried under reduced pressure for 1 h to yield 0.78 g of **2d** as a brown crystalline solid. Yield: 63.7%. ^1H NMR (C_6D_6, δ): 0.33 (s, 18H, $-Si(CH_3)_3$); 0.93 (d, 6H, $-CH_2CH(\mathit{CH_3})_2$); 1.10 (d, 6H, $-CH_2CH(\mathit{CH_3})_2$); 1.72 (m, 2H, $-C\mathit{H}_2CH(CH_3)_2$); 1.94 (m, 2H, $-C\mathit{H}_2CH(CH_3)_2$); 2.55 (m, 2H, $-CH_2C\mathit{H}(CH_3)_2$); 6.84 (t, 1H, *p*-NPh-*H*); 7.01 (m, 2H, aromatic); 7.12 (t, 2H, *m*-NPh-*H*); 7.31 (d, 2H, *o*-NPh-*H*); 7.36 (m, 2H, aromatic). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 2.20 ($-Si(CH_3)_3$, $J_{C-H} = 119.3$ Hz); 27.33 ($-CH_2CH(\mathit{CH_3})_2$, $J_{C-H} = 125.8$ Hz); 29.15 ($-CH_2CH(\mathit{CH_3})_2$, $J_{C-H} = 126.5$ Hz); 33.73 ($-CH_2\mathit{C}H(CH_3)_2$, $J_{C-H} = 127.2$ Hz); 80.01 ($-\mathit{C}H_2CH(CH_3)_2$); 121.79, 123.60, 125.46, 126.65, 128.62, 133.12, 155.97 (aromatic). Anal. Calcd for $C_{26}H_{45}N_3Si_2W$: C, 48.82; H, 7.09; N, 6.57. Found: C, 48.54; H, 7.11; N, 6.50.

Preparation of W(NPh)[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$](Ph)$_2$, 2e. $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](Cl)_2$ (1.0 g, 1.68 mmol) was dissolved in Et_2O (50 mL) and cooled to −78 °C. Two equivalents of PhMgCl (1.12 mL, 3.36 mmol; 3.0 M solution in Et_2O) were then added by a syringe. The reaction was allowed to warm to room temperature and was stirred for 2 h, during which time a brown color appeared and salts precipitated. The solvent was then removed under reduced pressure, and the remaining brown-orange solid was dried in vacuo for 3 h. The solid was then extracted with pentane and filtered by filter cannula until filtrate was almost clear. The solution was concentrated to about 10 mL and cooled to −78 °C for 3 h. The resulting orange solid was isolated by filtration and dried under reduced pressure for 1 h to yield 0.77 g of **2e** as an orange crystalline solid. Yield: 67.6%. ^1H NMR (C_6D_6, δ): 0.12 (s, 18H, $-Si(CH_3)_3$); 6.80−7.66 (19 H overlapping aromatic protons). Anal. Calcd for $C_{30}H_{37}N_3Si_2W$: C, 53.02; H, 5.49; N, 6.18. Found: C, 52.83; H, 5.44; N, 6.13.

Preparation of W(NPh)[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$](CH$_2$CH$_2$Ph)$_2$, 2g. $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](Cl)_2$ (2.0 g, 3.36 mmol) was dissolved in Et_2O (150 mL) and cooled to −78 °C. Two equivalents of $PhCH_2CH_2MgCl$ (3.4 mL, 3.4 mmol; 2.0 M solution in Et_2O) were then added by a syringe. The reaction was allowed to warm to room temperature and was stirred for 2 h, during which time a brown color appeared and salts precipitated. The solvent was then removed under reduced pressure, and the remaining brown-orange solid was dried in vacuo for 3 h. The solid was then extracted with pentane and filtered by filter cannula until the filtrate was almost clear. The solution was concentrated to ca. 10 mL and cooled to −78 °C for 3 h. The resulting orange solid was isolated by filtration and dried under reduced pressure for 1 h to yield 1.68 g of **2g** as a orange crystalline solid. Yield: 68.2%. ^1H NMR (C_6D_6, δ): 0.30 (s, 18H, $-Si(CH_3)_3$); 2.09 (dt, 2H, $-C\mathit{H}_2CH_2Ph$); 2.38 (dt, 2H, $-C\mathit{H}_2CH_2Ph$); 2.91 (dt, 2H, $-CH_2C\mathit{H}_2Ph$); 3.14 (dt, 2H, $-CH_2C\mathit{H}_2Ph$); 6.86 (t, 1H, *p*-NPh-*H*); 6.99 (m, 5H, aromatic); 7.02 (m, 2H, aromatic); 7.08 (t, 2H, *m*-NPh-*H*); 7.15 (m, 5H, aromatic); 7.22 (d, 2H, *o*-NPh-*H*); 7.39 (m, 2H, aromatic). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 1.48 ($-Si(CH_3)_3$, $J_{C-H} = 118.3$ Hz); 39.65 ($-CH_2\mathit{C}H_2Ph$, $J_{C-H} = 123.4$ Hz); 65.61 ($-\mathit{C}H_2CH_2Ph$, $J_{C-H} = 119.2$ Hz, $J_{W-C} = 77.2$ Hz); 122.83, 125.01, 125.20, 125.43, 125.58, 128.14, 128.48, 128.62, 132.95, 149.20, 156.22 (aromatic). Anal. Calcd for $C_{34}H_{45}N_3Si_2W$: C, 55.50; H, 6.17; N, 5.71. Found: C, 55.23; H, 6.09; N, 5.75.

Preparation of W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]$(CH_2Si(CH_3)_3)_2$, 2j. W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]$(Cl)_2$, **1** (2.0 g, 3.35 mmol), was dissolved in Et_2O (30 mL) and cooled to −78 °C. Two equivalents of $ClMgCH_2Si(CH_3)_3$ (5.23 mL, 6.70 mmol, 1.28 M solution in Et_2O) were then added. The reaction was allowed to warm to room temperature after 30 min. After 1 h, solvent was removed under reduced pressure. The solid was extracted with pentane until clear and filtered through a Celite pad. The solution was concentrated to a total volume of about 10 mL and cooled in a −78 °C bath to yield 1.98 g dark crystals of **2j.** Yield: 84.2%. ^1H NMR (C_6D_6, δ): 0.01 (s, 18H, $-CH_2Si(CH_3)_3$); 0.49 (s, 18H, $-NSi(CH_3)_3$); 1.32 (d, 2H, $-CH_2Si(CH_3)_3$); 1.96 (d, 2H, $-CH_2Si(CH_3)_3$); 6.85 (t, 1H, *p*-NPh-*H*); 6.91 (m, 2H, aromatic); 7.19 (t, 2H, *m*-NPh-*H*); 7.23 (m, 2H, aromatic); 7.52 (d, 2H, *o*-NPh-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 2.93 ($-CH_2Si(CH_3)_3$); 3.96 ($-NSi(CH_3)_3$, $^1J_{Si-C} = 56.8$ Hz); 63.64 ($-CH_2Si(CH_3)_3$); 119.91, 126.37, 127.92, 128.51, 128.58, 142.55, 155.59 (aromatic). Anal. Calcd for $C_{28}H_{47}N_3Si_2W$: C, 44.62; H, 7.06; N, 6.00. Found: C, 44.63; H, 7.02; N, 6.10.

Preparation of W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]$(CHCMe_3)(PMe_3)$, 3. In a 200 mL glass tube fitted with a Teflon J. Young's joint, W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$] $(CH_2CMe_3)_2$ (1.25 g, 1.87 mmol) was dissolved in toluene (25 mL). Five equivalents of PMe_3 (0.968 mL, 9.35 mmol) were then added, and the tube was sealed. The reaction was then heated to 80 °C for 24 h. The solution was transferred to a round-bottom Schlenk, and the solvent was removed under reduced pressure. The brown oil was extracted with pentane, and the volume of the filtrate was concentrated to ca. 15 mL. The solution was cooled to −10 °C to give 0.83 g of **3b** as orange crystals. Yield: 66.0%. ^1H NMR (C_6D_6, δ): 0.38 (s, 9H, $-Si(CH_3)_3$); 0.41 (s, 9H, $-Si'(CH_3)_3$); 0.98 (d, 9H, $-PMe_3$, $^2J_{W-C} = 9$ Hz); 1.39 (s, 9H, $-CMe_3$); 6.68−7.13 (m, 9H, aromatic). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 3.41 ($-Si(CH_3)_3$); 4.11 ($-Si'(CH_3)_3$); 16.22 (d, $-PMe_3$); 34.93 ($-CMe_3$); 45.04 ($-CMe_3$); 117.61, 119.32, 122.44, 123.56, 124.71, 128.71, 148.13 (aromatic); 277.41 ($-CHCMe3$, $^1J_{C-H} = 110$ Hz). Anal. Calcd for $C_{26}H_{46}N_3PSi_2W$: C, 46.49; H, 6.90; N, 6.26. Found: C, 46.23; H, 6.81; N, 6.05.

Preparation of W$(CH_2CH_2CH_2CH_2)$(NPh)[*o*-$(Me_3SiN)_2C_6H_4$], 4. W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]$(Cl)_2$ (1.05 g, 1.76 mmol) was dissolved in Et_2O (50 mL) and cooled to −78 °C. One equivalent of $BrMgCH_2CH_2CH_2CH_2MgBr$ (1.75 mL, 1.76 mmol; 0.99 M solution in Et_2O) was then added by a syringe. The reaction was allowed to warm to room temperature after 1 h and was stirred for another 2 h. The solvent was removed under reduced pressure, and the resulting solid was dried under reduced pressure for 3 h. The solid was then extracted with pentane and filtered through a Celite pad until the filtrate was almost clear. The solution was concentrated to about 10 mL and cooled to −78 °C for 2 h. The resulting golden solid was isolated by filtration and dried under reduced pressure for 1 h to yield 0.77 g of **4** as a brown solid. Yield: 75.2%. ^1H NMR (C_6D_6, δ): 0.28 (s, 18H, $-Si(CH_3)_3$); 1.54 (m, 2H, α-CH); 2.42 (m, 2H, β-CH); 2.91 (m, 2H, β-CH′); 2.93 (m, 2H, α-CH′); 6.86−7.44 (m, 9H, aromatic). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 1.08 ($-Si(CH_3)_3$, $^2J_{Si-H} = 6.6$ Hz, $J_{C-H} = 119.1$ Hz); 35.23 (β-C, $J_{C-H} = 124.3$ Hz); 61.25 (α-C, $J_{W-C} = 73.6$ Hz, $J_{C-H} = 122.9$ Hz). Anal. Calcd for $C_{22}H_{35}N_3Si_2W$: C, 45.43; H, 6.07; N, 7.23. Found: C, 45.19; H, 5.97; N, 7.03.

Preparation of W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]$(\eta^2-C_2H_4)(PMe_3)_2$, 5. In a glass tube with a Teflon J. Young's joint, W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]$(CH_2CH_3)_2$ **, 2b** (1.35 g, 2.32 mmol), was dissolved in pentane (50 mL). Five equivalents of PMe_3 (1.19 mL, 11.56 mmol) were added by a syringe, and then the flask was sealed. The reaction was stirred at room temperature for 4 h, during which time the brown solution turned purple and purple crystals precipitated. The mixture was transferred to a Schlenck tube, and the purple crystals were isolated. The mother liquors were reduced in volume under reduced pressure and cooled to −78 °C to give more solid. Total yield: 1.44 g, 88.3%. ^1H NMR (C_6D_6, δ): 0.31 (s, 9H, $-Si(CH_3)_3$); 0.60 (s, 9H, $-Si'(CH_3)_3$); 1.03 (s, 18H, $-PMe_3$); 1.91 (m, C_2H_4); 2.09 (m, C_2H_4); 6.61−7.42 (aromatic). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 2.67 ($-Si(CH_3)_3$); 6.34 ($-Si'(CH_3)_3$); 15.78 (s, $-PMe_3$); 38.13 (s, C_2H_4, $J_{C-H} = 156.2$ Hz); 122.23, 123.13, 124.28, 125.51, 127.23, 128.91, 129.23, 129.78, 158.23 (aromatic). Anal. Calcd for $C_{26}H_{49}N_3Si_2P_2W$: C, 44.25; H, 7.00; N, 5.95. Found: C, 43.91; H, 6.79; N, 5.78.

Preparation of W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$](CH*t*-BuCH_2CH_2), 8. W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]$(CHCMe_3)(PMe_3)$, **3** (1 g, 1.49 mmol), was dissolved in hexane (50 mL) and allowed to react with 16 psi of ethylene in the presence of excess neohexene at room temperature for 30 min. The solvent was removed under reduced pressure, and the resulting solid was dried under reduced pressure for 1 h. The solid was then extracted with pentane and filtered by cannula. The solution was concentrated to ca. 10 mL and cooled to −78 °C for 1 h. The resulting golden solid was isolated by filtration and dried under reduced pressure for 1 h to yield red orange solid at 54% yield. ^1H NMR (C_6D_6, δ): 0.24 (s, 9H, $-Si(CH_3)_3$); 0.26 (s, 9H, $-Si'(CH_3)_3$); 0.39 (m, 1H, $-CH'^tBuCH_2CH_2$); 0.71 (m, 1H, $-CH^tBuCH_2CH_2$); 1.21 (s, 9H, *t*-Bu); 2.45 (m, 1H, $-CH^tBuCH_2CH_2$); 2.61 (m, 1H, $-CH^tBuCH_2CH_2$); 3.75 (m, 1H, $-CH^tBuCH_2CH_2$); 6.82−7.44 (m, 9H, aromatic). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 1.35 (s, $-Si(CH_3)_3$); 1.54 (s, $-Si'(CH_3)_3$); 25.07 ($-CH^tBuCH_2CH_2$); 38.80 ($-CH^tBuCH_2CH_2$, $^1J_{W-C} = 49.4$ Hz); 77.58 ($-CH^tBuCH_2CH_2$, $J_{W-C} = 56.1$ Hz).

X-ray Crystal Structures. Data (Table 1) for both compounds were collected at 173 K on a Siemens CCD SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.710 73 Å). Cell parameters were refined using 8173 and 8192 reflections for **4** and **5**, respectively. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). Absorption corrections were applied on the basis of the ψ scan using the entire data set for **5** and on the basis of the measured crystal faces for **4**.

Both structures were solved by direct methods in SHELXTL5[20] and refined using full-matrix least squares on F^2. The non-H atoms were refined with anisotropic thermal parameters except for the disordered C atoms. All of the H atoms were included in the final cycle of refinement and were riding on the atoms to which they are bonded. The ethylene ligand in **4** was found to be disordered in the 2 and 3 positions. Two partial $-CH_2CH_2-$ groups were refined with isotropic thermal parameters and their occupation factors refined dependently to 0.54(2) for one and consequently 0.46(2) for the other. Atomic coordinates and equivalent isotropic displacement parameters of **4** and **5** can be found in the Supporting Information.

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Supporting Information Available: Tables of bond lengths and angles and positional and thermal parameters (17 pages). Ordering information is given on any current masthead page.

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[20] Sheldrick, G. M. *SHELXTL5*; Nicolet XRD Corp.: Madison, WI, 1995.